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Optical and electrical properties of vanadium oxide films deposited from alkoxides

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Vanadium oxide thin films are formed via the hydrolysis and condensation of vanadium alkoxides. Sol-gel chemistry provides a chemical control over condensation reactions and different materials are actually obtained depending on experimental conditions. The hydrolysis of vanadium alkoxide in the presence of an excess of water leads to ribbon-like particles of hydrated oxide V_2O_5.nH2O. Coatings with a preferred orientation are then deposited from these gels. They exhibit improved electrochemical properties as reversible cathodes for lithium batteries. Amorphous oxo-polymers are formed via the partial hydrolysis of vanadium alkoxides. They allow the deposition of optically transparent thin films that could be used in electrochromic display devices. Moreover, alkoxide derived films can be easily reduced into vanadium dioxide. These VO_2 thin films exhibit thermochromic properties. They exhibit the well known metal-insulating transition around 70°C. The transition temperature can be modified by doping with other metal cations.

Key words: Sol-gel, vanadium oxides, thin films, electrochromism, cathodes, thermochromism

Propiedades ópticas y eléctricas de películas de óxido de vanadio depositadas a partir de alcóxidos

Las películas delgadas de óxido de vanadio se formaron por la vía de hidrólisis y condensación de alcóxidos de vanadio. La química de sol-gel proporciona un control químico sobre las reacciones de condensación y los diferentes materiales se obtuvieron dependiendo de las condiciones experimentales. La hidrólisis del alcóxido de vanadio en presencia de exceso de agua conduce a partículas en forma de cinta de óxido hidratado de $V_2O_5.nH_2O$. Los recubrimientos con una orientación preferente fueron depositados a partir de los geles. Estos mostraron propiedades electroquímicas mejoradas como cátodos reversibles para báterias de litio. Oxo-polímeros amorfos se formaron por la vía de la hidrólisis parcial de alcoxidos de vanadio. Estos permiten la deposición de laminas delgadas ópticamente transparentes que pueden ser utilizadas como aplicaciones electrocrómicas en pantallas. Las películas derivadas de alcóxidos pueden ser fácilmente reducidas a dioxido de vanadio. Estas películas delgadas de VO_2 presentan propiedades termocrómicas y exhiben la bien conocida transición metal-aislante alrededor de 70°C. La temperatura de transición puede modificarse mediante dopado con otros cationes metálicos.

Palabras clave: Sol-gel, oxidos de vanadio, películas delgadas, electrocrómia, cátodos, termocromía.

1. INTRODUCTION

Sol-gel chemistry has been widely developed during the past decade for the processing of glasses and ceramics (1). It is based on the inorganic polymerization of molecular precursors such as metal alkoxides $M(OR)_z$. Hydrolysis and condensation reactions progressively lead to the formation of an oxide network (2). More or less viscous sol and gels are formed and one of the main advantages of the sol-gel route is to allow the powderless processing of glasses and ceramics (3). Thin films can be deposited directly from the solution, under ambient conditions, by such techniques as spin or dip-coating.

This paper describes the properties of vanadium oxide thin films deposited via the sol-gel route. These films exhibit both electronic and ionic properties and appear to be good candidates for the production of smart thin films. Electronic properties arise from the mixed valence behavior of vanadium oxide. Electron hopping occurs between metal ions in different oxidation states (V^V - V^{IV}) giving rise to semiconducting properties and specific optical absorption. Moreover, the hydrated oxide gel is formed of water molecules trapped within the vanadium oxide network. Ionic properties then arise from the acid dissociation of V-OH groups at the V_2O_5-H_2O interface (4).

The molecular design of alkoxide precursors provides a chemical control over condensation reactions allowing the synthesis of tailor made materials. Oriented thick coatings or optically transparent amorphous thin films can be obtained depending on the hydrolysis conditions. These vanadium oxide films could find applications for the realization of micro-batteries, electrochromic display devices or optical switches.

2. VANADIUM PENTOXIDE GELS, $V_2O_5.nH_2O$

2.1. Hydrolysis and condensation of vanadium alkoxides

Vanadium pentoxide gels $V_2O_5.nH_2O$ have been made via the hydrolysis and condensation of vanadium alkoxides $VO(OR)_3$ (R=Pr^i, Am^t). Such alkoxides are synthesized via the

reaction of ammonium vanadate with the corresponding alcohol as follows:

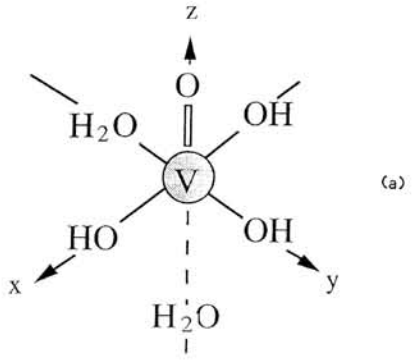
$$NH_4VO_3 + 3\ ROH \Rightarrow VO(OR)_3 + 2H_2O + NH_3 \qquad (OR = OPr^i, OAm^t)$$

The reaction is carried out in cyclohexane and the mixture is heated under reflux. Water is removed via azeotropic distillation. The vanadium alkoxide is purified by distillation under reduced pressure and then dissolved in its parent alcohol.

Vanadium oxide gels are then formed via the hydrolysis and condensation of these alkoxides as follows:

$$VO(OR)_3 + 3\ H_2O \Rightarrow VO(OH)_3 + 3\ ROH \qquad \text{(hydrolysis)}$$
$$2\ VO(OH)_3 \Rightarrow V_2O_5 + 3\ H_2O \qquad \text{(condensation)}$$

Actually the acid hydrolysis of $VO(OR)_3$ in the presence of an excess of water leads to the hexacoordinated neutral precursor $[VO(OH)_3(OH_2)_2]^0$ in which a weakly bonded water molecule lies along the z direction opposite to the short V=O double bond (Fig.1a). Condensation cannot occur along this z direction as there is no V-OH group. Condensation occurs only within the xy plane either via olation along H_2O-V-OH or oxolation along HO-V-OH. These two directions are not equivalent. Olation reactions usually proceed much faster than oxolation and condensation leads to ribbon-like oxide particles. Such ribbons can be clearly seen by electron microscopy (Fig.1b). They are about 0.5 μm long, 10 nm wide and 1 nm in thickness.



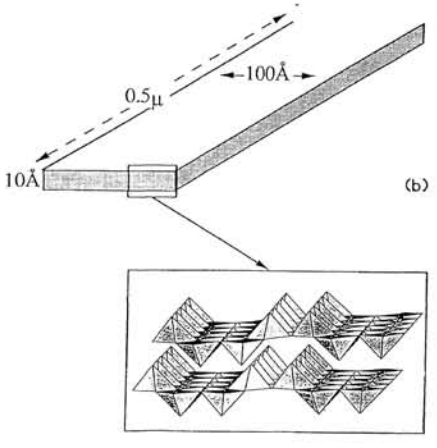


Fig. 1. *Synthesis of vanadium pentoxide gels V_2O_5,nH_2O. (a) neutral precursor $[VO(OH)_3(OH_2)_2]^0$, (b) schematic drawing of the oxide ribbons.*

When observed as thin layers (≈0.05 mm) by optical microscopy between crossed polarizers, vanadium oxide sols and gels display optical textures typical of nematic liquid crystals. This suggests that all the ribbons are aligned along the same direction giving a birefringent fluid phase. Such a nematic texture confirms the highly anisotropic structure of the oxide particles. Moreover, as shown by P. Davidson (5) $V_2O_5.nH_2O$ gels exhibit the 'banded texture' currently displayed by nematic polymers.

When deposited onto a flat substrate, vanadium pentoxide gels give rise to xerogel layers about 0.1mm in thickness that exhibit a preferred orientation. X-ray diffraction of these layers display the *00l* peaks typical of a turbostratic stacking of the V_2O_5 ribbons along a direction perpendicular to the substrate. The basal spacing between these ribbons increases when the amount of water increases, d= 8.8Å for n=0.5 and d=11.5Å for n=1.8. The shift Δd~2.8Å corresponds to the intercalation of one water layer between the ribbons (6-7).

Vanadium pentoxide gels, V_2O_5,nH_2O exhibit both ionic and electronic conduction (8). In the presence of an excess of water, acid dissociation of the V-OH groups occurs at the V_2O_5/H_2O interface leading to the formation of H_3O^+ species. Hydrated vanadium oxide gels then behave as polyvanadic acids $H_xV_2O.nH_2O$ (x~0.3). They exhibit fast proton conduction and the a.c. conductivity of thin films increases with the water content. When slightly reduced, vanadium pentoxide gels also exhibit electronic conduction arising from the hopping of unpaired electrons between V^{4+} and V^{5+} ions. Their electrical conductivity increases with the amount of V^{4+} ($\sigma_{300} \approx 4.10^{-5}$ $\Omega^{-1}cm^{-1}$ for V^{4+}=1%)

2.2. Electrochemical properties of vanadium oxide gels

Crystalline vanadium pentoxide V_2O_5 is known to be a promising candidate as reversible cathode for lithium batteries. Its redox potential is higher than 3 volts with reference to lithium and specific capacities as high as 125 Ah/kg could be obtained. The discharge curve of crystalline V_2O_5 exhibit several steps corresponding to the formation of different $Li_xV_2O_5$ phases (Fig.2a). However, despite its layered structure, this crystalline oxide behaves as a 3-D framework rather than a Van der Waals host and lithium insertion remains no longer reversible beyond the first two steps (x=1).

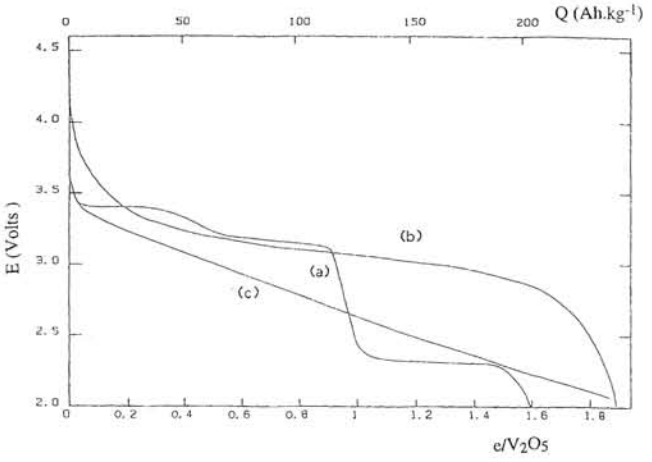


Fig. 2. *Discharge curve of V_2O_5 compounds. (a) crystalline oxide, (b) vanadium pentoxide xerogel, (c) amorphous oxopolymer.*

Chemical bonds between V_2O_5 ribbons in vanadium oxide gels are much weaker than in the crystalline oxide. Water molecules are intercalated in the interlamellar space and ionic species can diffuse easily through the oxide network. The electrochemical behavior of vanadium pentoxide gels $V_2O_5.nH_2O$ as a reversible cathode for lithium batteries is therefore quite different from that of the crystalline oxide (9). Moreover thin layers can be easily deposited onto various substrates allowing the fabrication of microbatteries.

The discharge curve of vanadium pentoxide xerogels exhibits a single plateau around 3.1V (Fig.2b). A faradaic yield close to 1.8 e/V_2O_5 and a capacity close to 250 $Ah.kg^{-1}$ are obtained at 2V corresponding to the reduction of all V^{5+} ions into V^{4+} (10). Cycling experiments show a good reversibility and almost 70% of the initial capacity is recovered after 30 cycles for a current density j=0.05 $mA.cm^{-2}$ (11). This improved behavior of gels should be due to the weak interactions between V_2O_5 layers allowing the reversible insertion of Li^+ ions between the ribbons rather than through the channels as for crystalline V_2O_5.

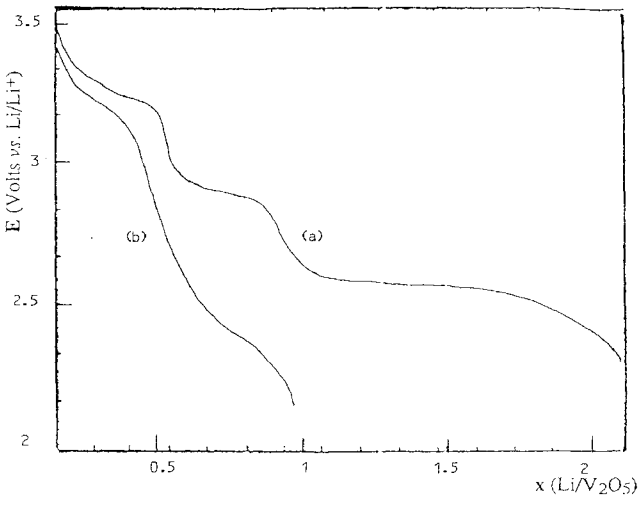


Fig. 3. *Discharge curves of β-$Na_{0.33}V_2O_5$. (a) oriented coatings prepared from vanadium pentoxide gels, (b) randomly oriented powder prepared via solid state reactions.*

2.3. Cation intercalation in vanadium oxide gels

Due to their layered structure, $V_2O_5.nH_2O$ gels behave as a versatile host for the intercalation of foreign species (6). A wide range of ionic or molecular species have been intercalated within these gels. Intercalation in V_2O_5 gels is much easier than with usual crystalline layered compounds. It occurs readily at room temperature within a few minutes when the xerogel is dipped into an aqueous solution of ionic salts. The internal structure of the oxide network and the 1-D stacking of the V_2O_5 ribbons are not destroyed. The basal distance increases and intercalation can be easily followed by X-ray diffraction (7). Intercalation mainly involves cation exchange reactions with the acidic protons of the gel. Na^+ intercalation for example leads to $Na_xV_2O_5,1.5H_2O$ (x~0.33). The layered structure is preserved with a basal distance d~11Å. This ordered stacking is not only preserved upon intercalation of Na^+ but also during a thermal treatment up to crystallization. Anisotropic coatings of vanadium bronzes β-$Na_{0.33}V_2O_5$ in which about 16% of the vanadium ions are in the reduced V^{4+} valence state were made upon heating $Na_{0.33}V_2O_5.1.5H_2O$ gels. These sol-gel bronzes crystallize around 350°C and exhibit the same monoclinic structure as the usual vanadium bronzes obtained via conventional solid state reactions at 700°C. However X-ray diffraction suggests that (a,c) planes are preferentially oriented parallel to the substrate while the tunnels of the bronze structure remain perpendicular to the substrate (12).

N. Baffier et al. (10-11) have shown that this preferred orientation of sol-gel layers could enhance the diffusion of Li^+ ions into the host lattice. The electrochemical insertion of Li^+, using $LiClO_4$ (1M) in PC as an electrolyte, takes place in the potential range 3.5-2.4 V (vs. Li/Li^+). Three well defined steps are observed corresponding to the filling of the different crystallographic sites of the bronze structure (Fig.3a). The influence of current density on the discharge curve clearly points out the better electrochemical performance of the sol-gel materials compared to the corresponding bronze prepared via solid-state reactions at 700°C (Fig.3b). Whatever the current density, the faradaic yield is almost twice larger, about 0.8 instead of 0.5 Li^+ per mole of bronze can be reversibly inserted into the sol-gel materials. This is probably due to the faster lithium diffusion through the oriented sol-gel film. The chemical diffusion coefficient of lithium (D_{Li} ~10^{-10} cm^2s^{-1} for 0<x<0.3) is almost two orders of magnitude larger than in the solid state derived bronze. The reversibility remains good in the potential range 3.8-1.8 V. A capacity of about 120 $Ah.kg^{-1}$ is still recovered after 50 cycles, twice the capacity obtained for solid state bronzes (13-14).

3. AMORPHOUS VANADIUM OXIDE THIN FILMS

As shown previously, the hydrolysis of vanadium alkoxides by a large excess of water leads to hydrated vanadium oxide gels. Olation and oxolation reactions along the «xy» plane lead to ribbons like particles and coatings exhibit a layered structure. Films deposited form these viscous V_2O_5,nH_2O gels are rather thick (≈0.1 mm). They are not transparent and cannot be used for optical applications. Moreover their adhesion onto glass substrates is not good enough.

Thin films can be easily deposited directly from alcoholic solutions of vanadium alkoxides by such techniques as spin-coating or dip-coating. No water is added to the alkoxide solution. The alkoxide film is left in air so that partial hydrolysis occurs spontaneously due to ambient humidity. The molecular precursors for condensation $VO(OR)_{3-x}(OH)_x$ are only partially hydroxylated and non hydrolyzed alkoxy groups prevent the formation of an oxide network. Oxo-polymers $[V_2O_{5-x}(OR)_x]_n$ rather than vanadium oxides are formed. Alkoxide solutions are much less viscous than vanadium oxide gels and thin films about 0.1 µm thick are obtained. Moreover, their adhesion to the substrate is much better than when $V_2O_5.nH_2O$ gels are used. This is due to the remaining alkoxy groups that can react with Si-OH groups at the surface of the silica substrate giving Si-O-V bonds.

As deposited thin films are optically transparent and appear to be amorphous by X-ray diffraction. They are pale yellow but turn green when dried under an infra-red heater around 60°C. Some reduction occurs due to the remaining organic components, and thin films contain more V^{IV} (V^{IV}/V^{V}~10%) than those deposited from aqueous solutions. As a consequence their electronic conductivity is higher (σ_{300} ~ $10^{-3}\Omega^{-1}cm^{-1}$).

The electrochemical properties of amorphous thin films deposited from vanadium alkoxides are quite different from those of layered $V_2O_5.nH_2O$ gels. A continuous decrease of the discharge curve rather than a large plateau is observed (Fig.2c). The open circuit voltage and the capacity are slightly smaller presumably because of the greater extent of reduction of V^V to V^{IV} during the synthesis.

Cyclic voltammograms also show different electrochemical behaviors depending on the sol-gel synthetic route. Cyclic voltammetry experiments were performed with a three-electrode electrochemical cell in the potential range -1.5,+1V (vs. Ag/Ag^+) and at a scanning rate of $10mV.s^{-1}$. The working electrode was made of a vanadium alkoxide thin film deposited onto a SnO_2:F electrode. The electrolyte was a solution of $LiClO_4$ (1M) in propylene carbonate. A platinum grid was used as the counter electrode and $Ag/AgClO_4$ as a reference. The voltammogram recorded with a $V_2O_5.nH_2O$ gel exhibits two peaks for both reduction and oxidation (Fig.4a). Li^+ ions are reversibly intercalated during the cathodic potential sweep and deintercalated during the anodic sweep. Such a behavior is close to that observed for crystalline V_2O_5 showing that these gels cannot be considered as amorphous. The charge inserted during the first cycle is 55 mC/cm^2, but it decreases rapidly upon cycling and only 8 mC/cm^2 are obtained after 10 cycles. The voltammograms recorded in the same conditions with amorphous films deposited from vanadium alkoxides exhibit featureless reduction and oxidation curves (Fig.4b). The charge inserted during the first cycle is smaller. This might be due to the larger amount of V^{4+} in the film. However insertion appears to be more reversible and a charge of 40 mC/cm^2 is still exchanged after 20 cycles.

Vanadium oxide films can be easily doped by mixing two alkoxides in the precursor solution. Amorphous thin films were then obtained via the deposition of a mixture of $VO(OAm^t)_3$ and $Ti(OPr^i)_4$ (90%-10%) in Pr^iOH. They exhibit improved properties, 62 mC/cm^2 are inserted during the first cycle and still 56 mC/Cm^2 after 20 cycles. This protective mechanism could be due to the preferential reduction of Ti^{IV} rather than V^{IV} near the low voltage limit preventing any over-reduction into V^{III} (15).

Optical absorption measurements performed during cyclic voltammetry experiments show that the coloration of amorphous thin films changes progressively during the reduction-oxidation cycle. They turn from yellow to green, gray and blue upon reduction. The process is highly reversible and optical switching occurs within few seconds when a voltage of ± 2V is applied (16). Optically transparent thin films deposited from vanadium alkoxides could therefore be used for the realization of electrochromic devices. However their absorption in the visible optical spectrum is quite low when the film is very thin (~0.1μm). This suggests that they should rather be used as counter electrodes in electrochromic devices (17).

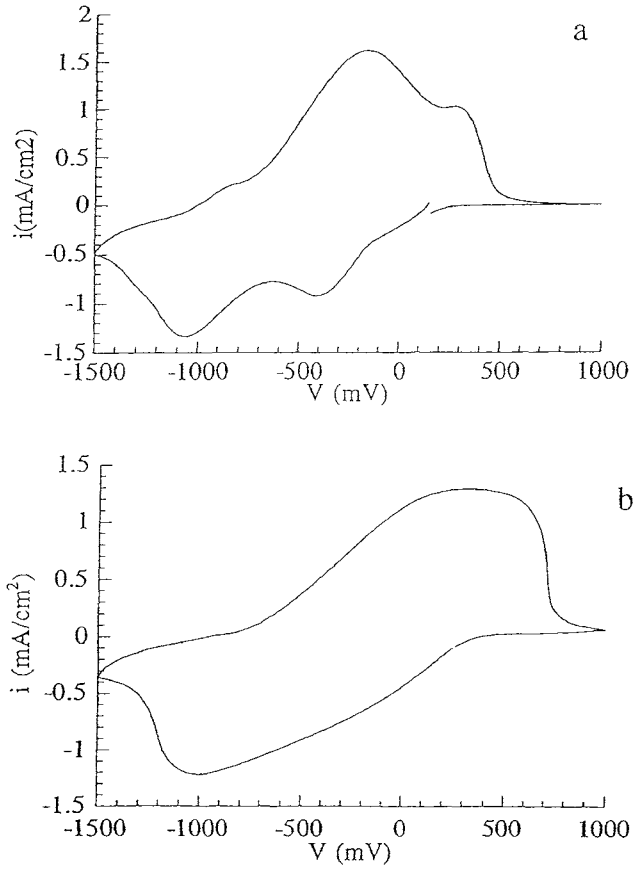


Fig. 4. *Cyclic voltammograms of vanadium oxide thin films. (a) $V_2O_5.nH_2O$ gels, (b) amorphous vanadium oxopolymers.*

4. THERMOCHROMIC VO_2 THIN FILMS

Vanadium dioxide VO_2 is known to undergo a reversible semiconductor-metal transition at 68°C (18). The high temperature phase has a tetragonal rutile type structure characterized by chains of edge sharing $[VO_6]$ octahedra along the c axis with equidistant vanadium atoms (V-V=2.88Å). Vanadium pairing occurs below 68°C giving rise to a monoclinic phase with alternate shorter (2.65Å) and longer (3.12Å) V-V distances. This V-V pairing opens a gap at the Fermi level in the t_{2g} band. It is accompanied by an abrupt shift in resistivity as well as in optical properties. Above 68°C electrical conductivity increases abruptly and vanadium dioxide becomes metallic and infrared reflecting.

The switching temperature for VO_2 is nearer to room temperature than for any other compounds, which accounts for the interest in this oxide for applications such as smart windows, thermal sensors and optical or electrical switching devices.

Most fundamental studies have been performed on VO_2 single crystals. However the structural distortion associated with the crystallographic transition prevents the use of bulk materials for practical applications. VO_2 crystals break after few cycles. Thin films appear to be able to survive stresses during repetitive cycling around the transition and would be much more convenient for optical applications.

4.1. Sol-gel synthesis of VO_2 thin films

Vanadium dioxide thin films have already been made from V^{IV} alkoxides $V(OR)_4$ (19). However these alkoxides are rather difficult to synthesize and highly reactive toward hydrolysis and oxidation. Therefore V^V oxoalkoxides $VO(OR)_3$ would be much more convenient precursors. Optically transparent amorphous thin films are deposited from alkoxide solutions

and crystalline phases are formed upon heating. V_2O_5 films are obtained in air whereas reduced phases are formed in the presence of hydrogen. The pure VO_2 phase is obtained when the film is heated for two hours at 500°C under a reducing gas flow (Ar-H_2 5%). These crystalline VO_2 thin films exhibit a good optical quality. Scanning electron microscopy shows that these films are made of rather monodispersed and uniformly distributed VO_2 particles about 100 nm in size (20).

4.2. Electrical switching of VO_2 thin films

Conductivity measurements performed on crystalline VO_2 films show that their electrical resistance drops by almost three order of magnitude above 70°C (Fig.5a). A typical heating-cooling hysteresis effect of about ±10°C is observed. It is of the same order of magnitude as those usually observed on VO_2 thin films.

Sol-gel deposited VO_2 thin films can be used for making electrical switches (21). The switching device is simply made via the deposition of gold electrodes, 0.4 mm apart, at the surface of the VO_2 film. These electrodes are evaporated through a mask so that the geometry of the inter-electrodes space can be accurately controlled. An a.c. voltage is applied to the device and the current-voltage (*I-V*) curve is recorded onto an oscilloscope (Fig.5b). Along the OA line, the device follows an Ohm's law, V=RI. The film is in the insulating «OFF» state and its resistance is quite high. However as the current increases, the film is heated via the Joule effect. At a given threshold voltage (V_{th}~50V) the temperature of the film becomes larger than its transition temperature and the vanadium dioxide becomes metallic «ON» state and its resistance drops by a factor of about 10^3. The voltage decreases while the current increases (line AB). The device remains in the «ON» state as long as its temperature is higher than the transition temperature *i.e.* as long as the current is larger than the holding current I_h~0.6 mA (point C). Beyond this point, the film switches back to the «OFF» state (line CO).

4.3. Optical switching in VO_2 thin films

The optical transmission of VO_2 thin films was measured in the infra-red at a wavelength λ=2.5μm in the temperature range 15°C-100°C. IR transmittance also exhibits a typical hysteresis loop around the transition temperature (Fig.6). For pure VO_2 films, optical switching occurs around 80°C upon heating and below 60°C upon cooling. In the metallic state, optical transmittance drops by almost two orders of magnitude and becomes smaller than 1% suggesting that the reflectivity of VO_2 films is quite high (Fig.6a).

The transition temperature T_c of VO_2 can modified by doping. According to literature it decreases with high-valent cations (Nb^{5+}, Mo^{6+}, W^{6+}) and increases with low-valent

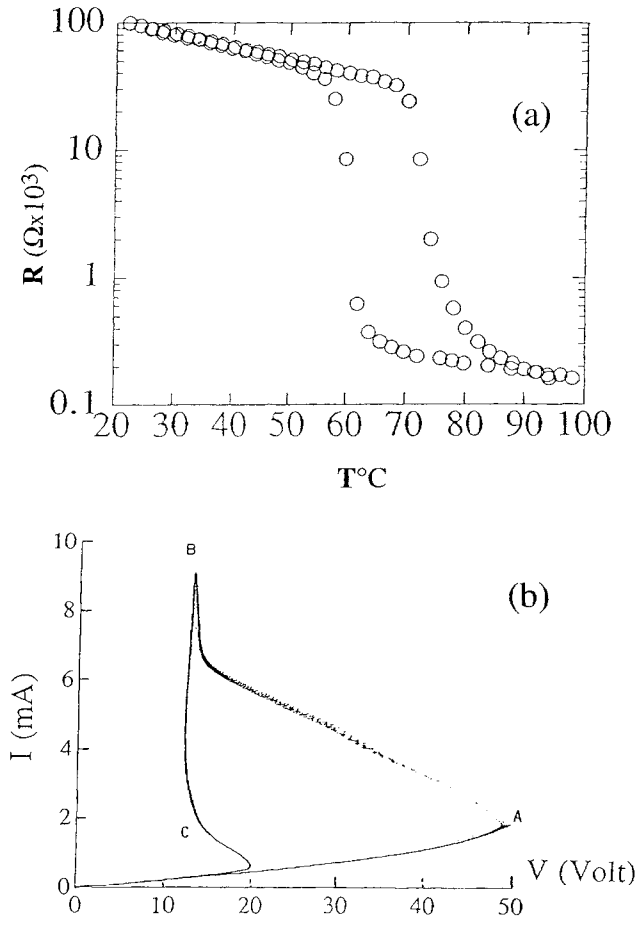


Fig. 5. *Electrical switching of sol-gel deposited VO_2 thin films. (a) temperature dependence of the resistance, (b) current-voltage characteristic at room temperature.*

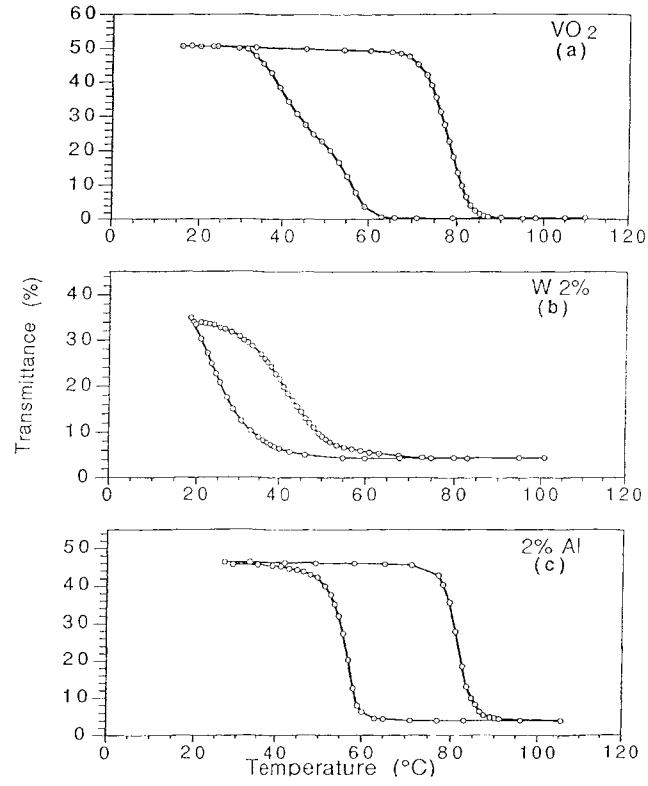


Fig. 6. *Optical switching in M_xVO_2 films in the infra-red (λ=2.5 μm). (a) VO_2, (b) $W_{0.02}VO_2$, (c) $Al_{0.02}VO_2$.*

dopants (Al^{3+}). Doped M_xVO_2 ($M = W^{6+}$, Al^{3+}) thin films have then been made by adding a given amount of molecular precursor such as $WOCl_4$ or $Al(OBu^s)_2(etac)$ ($etac=C_6H_9O_3$) to the vanadium alkoxide solution. The mixed solution is then deposited by spin-coating and heated as previously.

As expected the temperature at which the optical switching occurs is significantly smaller, around 40°C upon heating, when the film is doped with 2% of W^{VI} (Fig.6b). Transition close to ambient temperature can even be obtained when the amount of W^{VI} reaches 5%. The reverse is observed with Al^{III} doped VO_2 films for which the optical switching occurs around 90°C upon heating (Fig.6c).

CONCLUSION

This paper describes the properties of vanadium oxide thin films deposited via the sol-gel route. It shows that starting from a given precursor, $VO(OR)_3$, different films can be obtained depending on the experimental procedure. Sol-gel chemistry provides a chemical control over hydrolysis and condensation reactions allowing the synthesis of tailor-made materials. The chemical nature and structure of these films can be optimized depending on the desired application, reversible cathode, electrochromism, or thermochromism.

This paper only describes some applications. Other vanadium oxide gels have been reported in the literature. Highly porous aerogels have been obtained upon hypercritical drying of vanadium oxide gels. They are able to intercalate almost two Li^+ per V_2O_5 with good cycling properties (22). New hybrid materials have also been obtained in which organic molecules are intercalated within the layered structure of $V_2O_5.nH_2O$ gels. This field was initiated by Kanatzidis et al. (23) who performed the in situ intercalation/polymerization of conducting polymers such as polyaniline or polythiophene. More recently, the glucose oxidase enzyme, was encapsulated within $V_2O_5.nH_2O$ gels and used as an active electrode for the realization of biosensors (24).

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